

## SELECTIVE PARTIAL OXIDATION OF METHANE BY CATALYTIC SUPERCRITICAL WATER OXIDATION

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### ABSTRACT

The product spectrum obtained from catalytic partial oxidation in supercritical water has been compared to that obtained from catalytic oxidation in the gas phase. The presence of supercritical water inhibits the methane conversion but promotes the yield of methanol. The effect of oxygen concentration on the reaction in supercritical water has also been considered. High oxygen concentrations apparently inhibit the conversion reaction and decrease the yield of methanol. These results are considered in terms of consistent reaction pathways.

Keywords: Methane, Partial Oxidation, Supercritical Water

### INTRODUCTION

Abundant supplies of natural gas exist within the United States. Methane, the major component of natural gas, is useful primarily as a fuel and, because it is difficult to transport, primarily at the wellhead. Partial oxidation to methanol or formaldehyde, or oxidative coupling to ethylene or other higher hydrocarbons, would greatly enhance the usability of methane both as a fuel source and as a raw material. Unfortunately, it is easier to convert partial oxidation products such as methanol to complete oxidation products than it is to form the partial oxidation products in the first place.

Research has centered on the identification of a selective catalyst which will provide high selectivity to partial oxidation products. Limited success has been obtained using selected metal-oxide catalysts, namely  $\text{MoO}_3$  and  $\text{Cr}_2\text{O}_3$  [Pitchai & Klier, 1986]. However, in these cases low conversion must be maintained so that the desired methanol product is not further converted to undesired complete oxidation products. The complete oxidation products, CO and  $\text{CO}_2$ , have little economic value. Low oxygen concentrations also have been used to increase the selectivity to partial oxidation products. Reports also indicate that, independent of the catalyst, the addition of water decreased the rate of methane conversion but increased the selectivity to methanol [Pitchai & Klier, 1986].

The use of supercritical water as a reaction solvent has previously been shown to alter the reaction pathways and thereby the product spectrum. Kinetic studies for the thermal oxidation of carbon monoxide, ammonia, and ethanol in supercritical water [Helling & Tester, 1987; Helling & Tester, 1988] revealed that secondary reaction pathways can be created through the addition of the supercritical fluid. Thermal oxidations of methane and methanol were accomplished in supercritical water [Rofer &

Streit, 1989] and a mechanism, modified from the gas-phase free radical mechanism, approximately described the kinetics. Extrapolation of the kinetics obtained from these experiments reveals that high methanol yields should be obtained from thermal oxidation in supercritical water [Dixon & Abraham, 1991].

Several investigators have also demonstrated that the addition of a supercritical fluid in a catalyzed reaction can influence the mechanism through which conversion is obtained. In one particular effort of interest, Dooley & Knopf [1987] selectively converted toluene to benzaldehyde through oxidation over  $\text{CoO}/\text{Al}_2\text{O}_3$  in supercritical  $\text{CO}_2$ . In the oxidation of cumene hydroperoxide, Suppes & McHugh [1989] have shown that the addition of the catalyst can promote specific steps in a free-radical mechanism relative to others, which led to an observed change in the product selectivity.

Within the current paper, we present evidence to indicate that oxidation of methane in the presence of supercritical water can be used to promote the formation of the desired partial oxidation product, methanol. Gas phase catalytic oxidation is compared with catalytic oxidation in supercritical water, in terms of both methane conversion and methanol yield. Secondly, the influence of oxygen concentration on the conversion and methanol yield is considered.

## EXPERIMENTAL

Batch reactions were used to determine the influence of supercritical water on the product spectrum of catalytic oxidation of methane. All reactions were carried out in separate 1.26 mL batch reactors, which have been described in detail elsewhere [Jin & Abraham, 1990]. Each reactor was loaded at room temperature with 0.8 mg of  $\text{Cr}_2\text{O}_3$  catalyst [Aldrich Chemical]. For the reactions with supercritical water, 0.4 g deionized water was also added to the reactor. After the reactors were sealed, oxygen, methane, and nitrogen were added to the reactor in the desired proportions to a total pressure of 51.7 bar; for the high oxygen concentration study, a gas mixture containing 1.83% methane, 18.4%  $\text{O}_2$  and the balance nitrogen [Scott Specialty Gases] was used. All materials were commercially available and used as received.

After loading, the reactors were placed into a high temperature fluidized sandbath (Tecam SBL-2), which had been pre-heated to the desired temperature. After the desired reaction time, the reactor was quenched by placing it into a cold water bath. Insertion into the sandbath and into the cold water bath corresponded to zero and the measured reaction time, respectively. Each experiment was repeated at least twice and the resulting values averaged to obtain the reported data. Heatup time for these reactors was approximately 1 minute, short compared to ultimate reaction times of up to 40 minutes.

The small reactor size, combined with the high temperature and pressure at the reaction conditions made measurement of the actual reaction pressure unfeasible. However, it was possible to estimate the actual pressure of the gas phase reaction using the assumption of the ideal gas law; this provided an estimate of the pressure as 118.8 bar. For the reactions in supercritical water, the actual pressure at the reaction temperature of 400 °C was greater than the gas phase reactions. Steam tables could be used to estimate the partial pressure of water at the reaction conditions as 325 bar, and then assuming Dalton's Law allows estimation of the total pressure as 444 bar.

Product analysis was accomplished by gas chromatography. For the gas analysis, an Hewlett Packard 5840 gas chromatograph with gas sampling valve, 30 ft Haysep DB packed column, and thermal conductivity detector, was used in temperature programmed mode. Liquid analysis was accomplished with the HP 5840 instrument, using capillary column injection, 10 m DB-5 capillary column, and flame ionization detector. In both cases, product identification was accomplished by injection of pure component samples of the suspected material. Quantification was accomplished by comparison of peak areas with that of a standard, calibrated by injection of known amounts of materials. Inert nitrogen introduced with oxygen as air was the standard for the gas phase products while added naphthalene was used as a liquid phase standard.

## RESULTS AND DISCUSSION

The conversion of methane is reported as a function of time in Figure 1, in which the gas phase conversion is compared directly with catalytic oxidation in supercritical water. Conversion increased monotonically with time in both cases. For the gas phase catalysis, approximately 0.6 conversion was achieved at 40 minutes, compared with approximately 0.3 conversion for the supercritical water case. At any given reaction time, the conversion achieved from gas phase catalysis was approximately twice that obtained from the reaction in supercritical water.

Experiments were accomplished at 400 °C and initial concentrations of oxygen and methane of 6.32 mol/L and 0.627 mol/L, respectively. The stoichiometry of the complete combustion reaction



indicates that only 2 moles of oxygen are required for complete conversion of methane to  $\text{CO}_2$  and water. Thus, initial experiments were accomplished with greater than 500% excess of oxygen and should be well-represented by assuming that the kinetics are independent of oxygen concentration. Pseudo-first order kinetics for methane conversion provides

$$dx/dt = k(1-x) \quad (2)$$

which upon integration reveals

$$x = 1 - \exp(-kt) \quad (3)$$

Best fit analysis of the data of Figure 1 in terms of equation 3 provides estimated values of the rate constants as  $0.0233 \text{ min}^{-1}$  and  $0.0115 \text{ min}^{-1}$  for gas and supercritical water phase reaction, respectively. The solid lines in Figure 1 represent the predictions of the first order approximation and indicate the quality of the fit of the data.

Methanol yield is compared for the two cases in Figure 2. Essentially no methanol was observed for the gas phase catalysis at any reaction time. For the case of oxidation in supercritical water, the methanol yield ( $y_{\text{MeOH}} = C_{\text{MeOH}}/C_{\text{CH}_4,0}$ ) was also low, however, a maximum of approximately 0.7% yield was obtained at 5 minutes. The concentration decreased at longer reaction times, owing to subsequent conversion of methanol to complete combustion products  $\text{CO}_2$  and water. Although the oxygen

concentration was in substantial excess, thereby favoring the production of total oxidation products, the yield of methanol was increased by more than one order of magnitude through the presence of the water. The lines in Figure 2 do not represent kinetics predictions but are used to more clearly indicate the trends in the data.

The presence of supercritical water serves to inhibit the initial conversion of methane, as evidenced by the data of Figure 1. This may occur by inhibiting adsorption of either methane or oxygen (or both), thereby decreasing the available concentration of the reactants. Alternatively, water may compete with the reactants for catalytic sites, or may poison some sites, limiting the effectiveness of the catalyst. It is not clear, however, what effect the water has on the reaction of methanol to  $\text{CO}_2$  and water. Certainly, the presence of water promotes the formation of methanol, as indicated in Figure 2. From this observation, it would be suspected that the presence of water inhibits conversion of methanol to  $\text{CO}_2$  and water, as well. The mechanism of this inhibition, while not determined within this study, could be attributed to the same factors used in understanding the inhibition of the methane conversion reaction.

Initial experiments were accomplished at high oxygen concentration, which would be expected to promote methane conversion but inhibit the formation of methanol. Several experiments were then accomplished to determine the effect of oxygen concentration on methane conversion and methanol yield. In these cases, the molar ratio of oxygen to methane is indicated in terms of the initial loading in the reactor,  $\theta = \text{C}_{\text{O}_2}/\text{C}_{\text{CH}_4}$ . Based on this definition and the stoichiometry of equation 1,  $\theta = 2$  would correspond to stoichiometric oxygen.

Figure 3 reveals the effect of oxygen concentration on the methane conversion. At very low oxygen concentration,  $\theta = 0.071$ , conversion increased to approximately 0.1 after 5 minutes, and then remained steady at longer reaction times. In this case, the maximum conversion based on the stoichiometry and the oxygen loading should be approximately 0.035. However, if only methanol is produced, the reaction stoichiometry is



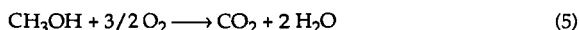
and, given the oxygen loading, 0.14 conversion could be expected. Thus, it was likely that this low oxygen concentration reaction was oxygen-limited.

For oxygen concentration  $0.6 < \theta < 0.8$ , conversion increased steadily with reaction time, reaching approximately 0.25 conversion at 20 minutes. Little discrimination in conversion could be observed between the 3 experimental runs attempted within this concentration range. The high oxygen concentration data is repeated from Figure 1 for comparison purposes and reveals that conversion was slightly lower at  $\theta = 8.72$  than at the lower concentration conditions. Although this was not expected, it is possible that the high concentration of oxygen inhibited methane conversion by preferential adsorption of oxygen onto the catalytic sites.

The effect of oxygen concentration on the yield of methanol is indicated in Figure 4. In all cases, a maximum in methanol yield was observed at a reasonable short reaction time. The highest yield was observed for  $\theta = 0.071$ , with a maximum yield of approximately 0.035 at 10 minutes. Considering that methane conversion was only 0.12 at this reaction time, the selectivity to methanol ( $s = y/x$ ) was approximately 30%. As

the oxygen concentration was increased, the maximum yield of methanol decreased. For the intermediate range of oxygen,  $0.6 < \theta < 0.8$ , the maximum yield was approximately 0.015 at 15 minutes, and the maximum methanol yield was 0.005 for the high oxygen concentration case.

These observations for methanol yield are consistent with a series of reaction pathways described by equation 4 above followed by further reaction of methanol to  $\text{CO}_2$  and water,



From Figure 4, this reaction is likely to be dependent upon the oxygen concentration, with higher concentrations of oxygen promoting methanol conversion. The data of Figure 3 suggests that the initial conversion of methane to methanol is essentially independent of oxygen concentration, although at high concentration, oxygen apparently inhibits the initial conversion. Under all conditions, reaction 5 is more facile than is reaction 4, leading to low methanol yield in all cases. However, the yield of methanol is greater in all cases where supercritical water was present than when the reaction was accomplished within the gas phase.

## CONCLUSIONS

Methane oxidation was inhibited by the presence of supercritical water, with the rate of reaction being approximately one-half of that observed for gas phase oxidation.  $\text{CO}_2$  and water were always the primary products of the reaction, but methanol was formed as an intermediate in low to moderate yield. The presence of supercritical water increased the yield and selectivity of methanol by approximately one order of magnitude compared to reaction in the gas phase. Little effect of increasing oxygen concentration was observed on the methane conversion reaction occurring within supercritical water, although inhibition was observed at very high oxygen concentration. At all oxygen concentrations, increasing oxygen led to a decrease in the maximum yield of methanol.

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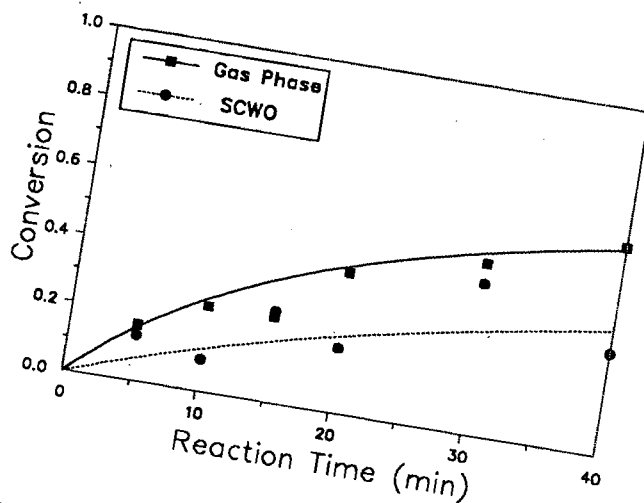


Figure 1: Comparison of methane conversion obtained from gas phase and supercritical water catalytic oxidation at 400 °C.

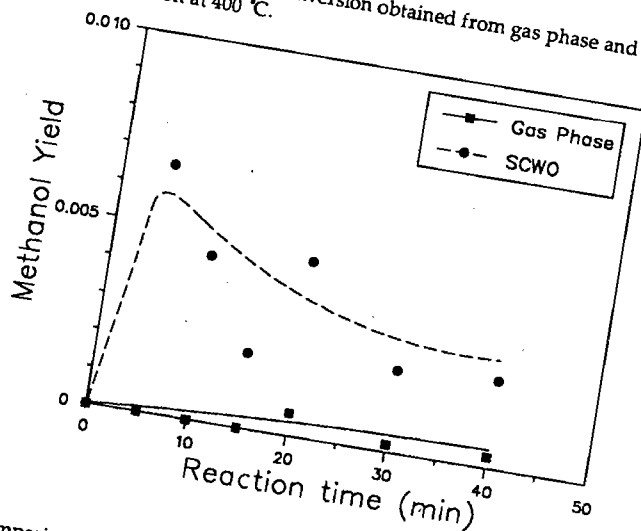
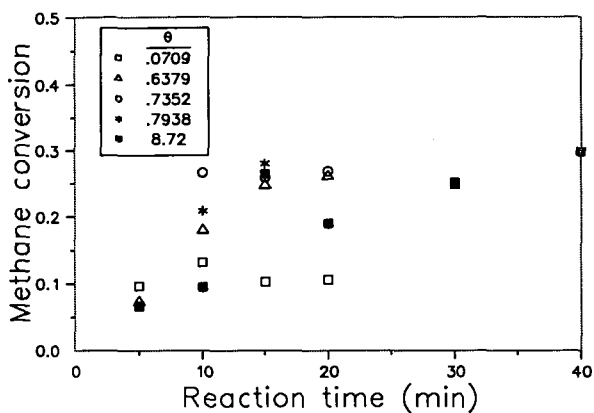
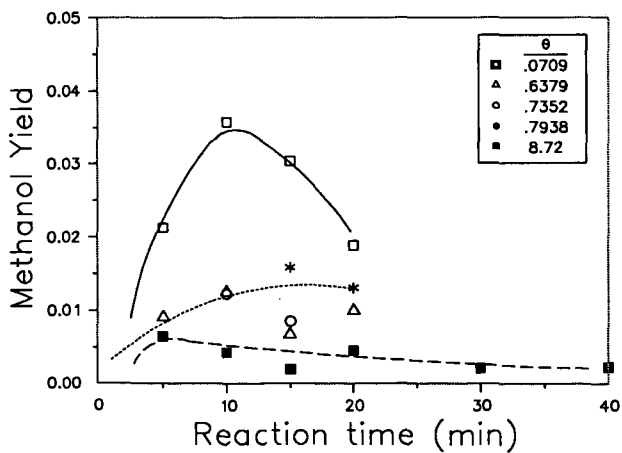


Figure 2: Comparison of methanol yield obtained from gas phase and supercritical water catalytic oxidation at 400 °C.



**Figure 3:** Influence of oxygen concentration on the temporal variation of methane conversion during catalytic oxidation in supercritical at 400 °C.



**Figure 4:** Influence of oxygen concentration on the temporal variation of methanol yield during catalytic oxidation of methane in supercritical at 400 °C.